Kelco
Biopolymers

PECTIN

CHEMISTRY, FUNCTIONALITY, & APPLICATIONS

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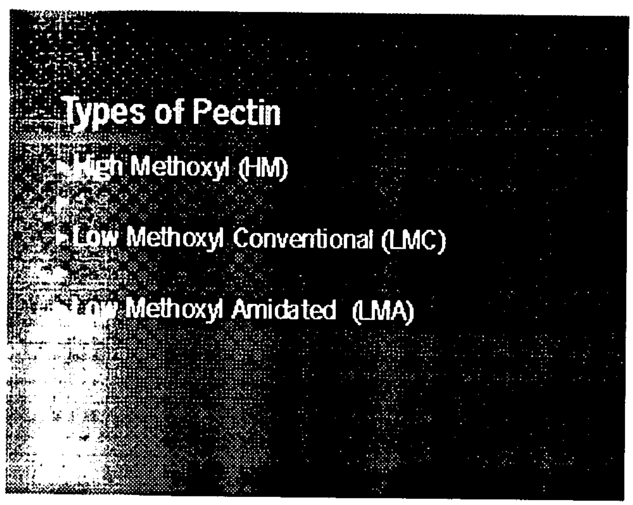
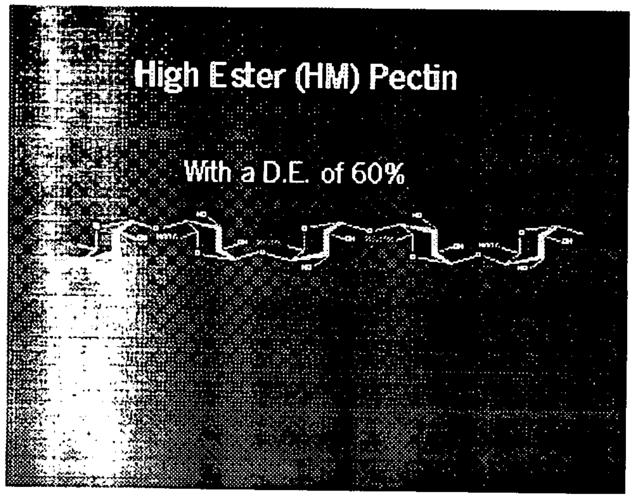
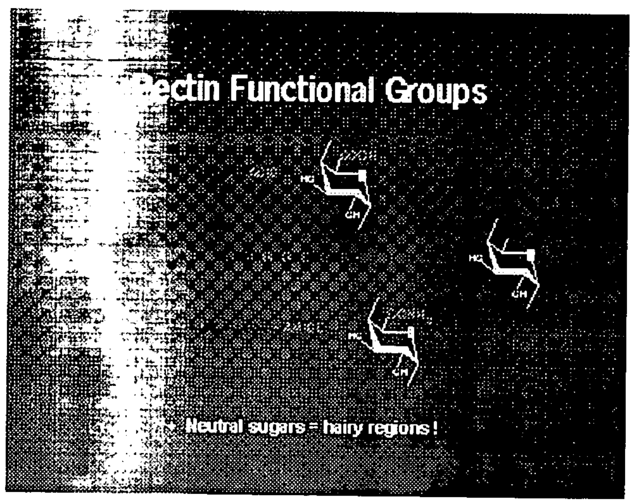
In this lecture all types of pectin will be discussed, however the emphasis will be on LM pectin, as this is the most misunderstood yet most versatile type of pectin. Applications of both types of pectin in food systems will be covered at the end of the talk.



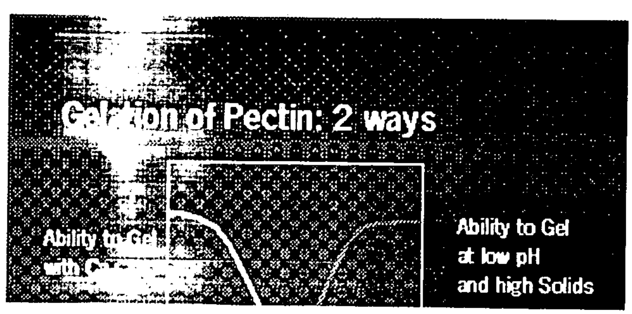
Pectin is divided into two main categories: HM pectin and LM pectin (Figure 1). The LM pectins are further subdivided into two groups: low methoxyl amidated (LMA), and low methoxyl conventional (LMC). The reasons for these three classes of pectin will become clear as we get into the chemistry of pectin. Some biochemistry will be covered at the beginning of the talk, but no more than is necessary for your understanding of why pectin behaves the way it does.

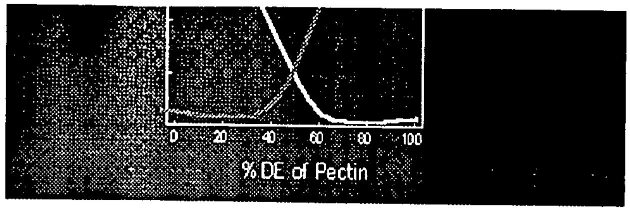


Pectin is the methylated ester of polygalacturonic acid. It is commercially extracted from citrus peels and apple pomace under mildly acidic conditions. Figure 2 shows a portion of a pectin molecule. Each ring is a molecule of galacturonic acid, and there are 300 to 1000 such rings in a typical pectin molecule, connected in a linear chain. You can see five such galacturonic acid units in Figure 2. Please note that three of the five are in the methyl ester form, while the other two are in the acid form. This represents a degree of methoxylation of 3 out of 5, or 60 percent. You will see the term abbreviated as "DM" or "DE", which is short for degree of esterification. Both terms are interchangeable, and they refer to the percentage of acid groups which are present in the pectin molecule as the methyl ester.

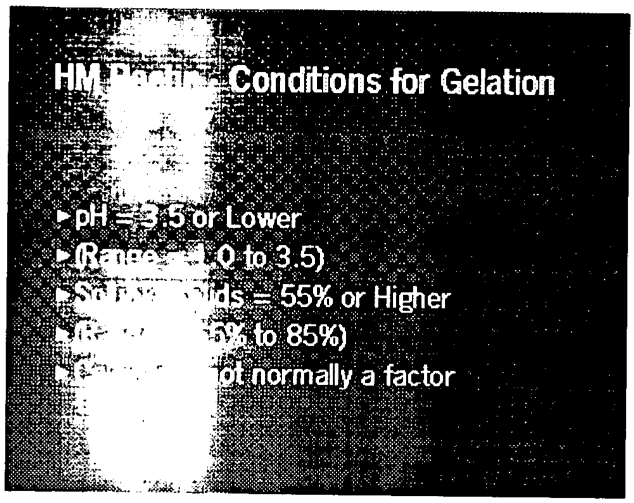


The "business end" of the pectin molecule is it's carboxyl acid group. As seen in Figure 3, the only difference between HM pectin and LMC pectin is in the relative proportions of acid and ester groups, yet it is this difference that causes them to gel under completely different conditions. The LMA pectins may have up to 25% amide groups, and this changes their texture and temperature characteristics, which will be explained a little further on.





By FCC definition, any pectin of 50% DE or greater is a High Methoxyl pectin, while anything under a DE of 50% is low methoxyl pectin. The two types of pectin will gel for completely different reasons, as indicated in Figure 4. HM pectin gels due to high soluble solids and low pH conditions, as indicated on the graph as a solid line. As the DE of a pectin is lowered, it begins to lose it's ability to gel under these conditions. The dotted line is for the ability to gel with divalent ions (usually calcium ions in food systems). This is the hallmark of LM pectin. Please note that as the DE is raised, the pectin will eventually lose it's ability to gel with calcium. Also note that a pectin with a DE around 50% will posses characteristics of both



The bare minimum conditions for causing H 1 pectin to gel are shown in Figure 5. If your system is not at least 55% solids AND has a pH of 3.5 or lo) HM pectin will not gel, no matter how much of it you add to your product. I'm not saying that HM 't used under these conditions, but if it is, then it is not a gelling agent but a thickening agent. From e can see that the range of gelling conditions for HM pectin are a pH of 1.0 to 3.5, and a solids range) 85%. Also note that the presence or absence of calcium ions is not normally a factor for HM pectin except in special cases.

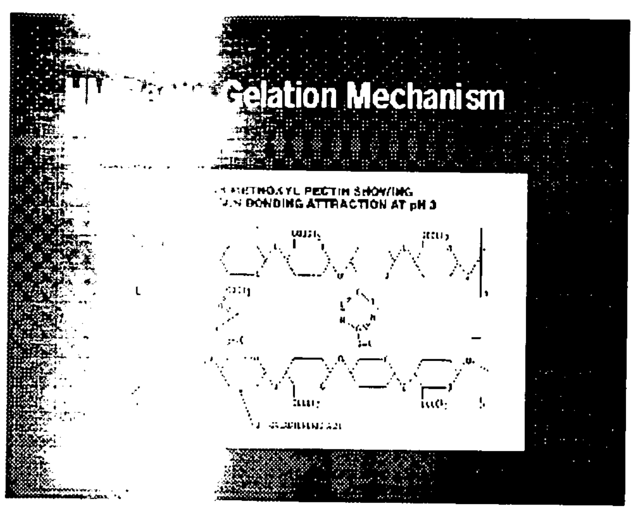
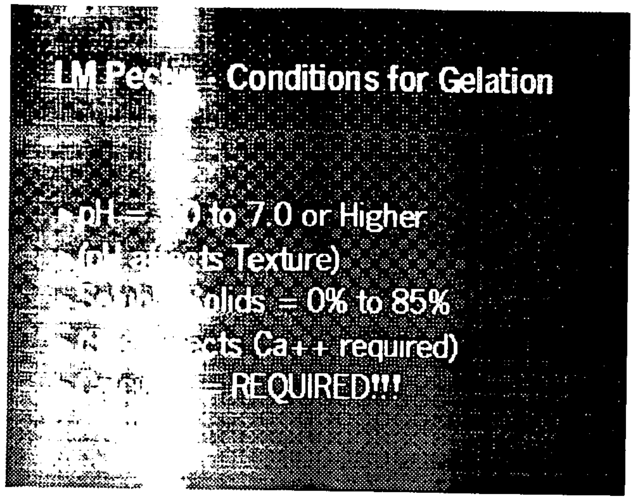


Figure 6 illustrates the mechanism of ge for HM pectin. At a pH of 3.0, about 90% of the available acid groups are not dissociated, and are apable of hydrogen bonding to acid or hydroxyl groups on

adjacent chains. These "junction zones" co[illegible]ld be thought of as crystallized out of solution, while the non-cross linked portions of the molecules are still in [illegible]lution. Therefore, it could be said that an HM pectin gel is literally half in and half out of solution.



The gelling range of conditions for LM pe[illegible] is illustrated in Figure 7. The good news is that LM pectin gels over a wider pH range than HM pectin, [illegible]y pH = 1.0 to 7.0 or higher. pH does influence the texture of the gel, which I will explain later. Also, the s[illegible] solids or Brix gelling range for LM pectin is much wider than HM pectin. One can gel LM pectin fro[illegible] 80% solids. The bad news is that you have one more parameter to keep track of, and that is the calciu[illegible]nt of your product. "No calcium, no gel" with LM pectin. Fortunately, this is not as difficult as it so[illegible], and this will be made clear shortly.

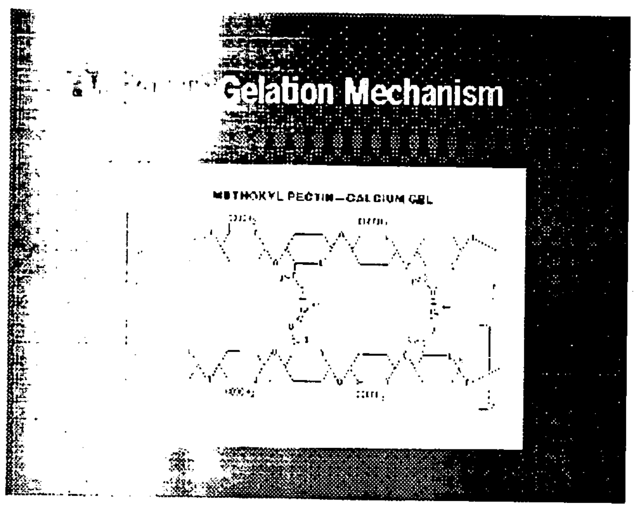
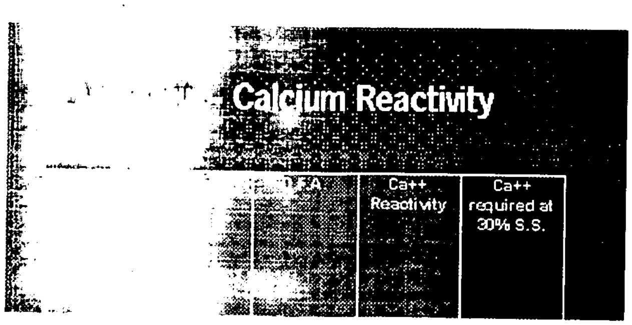
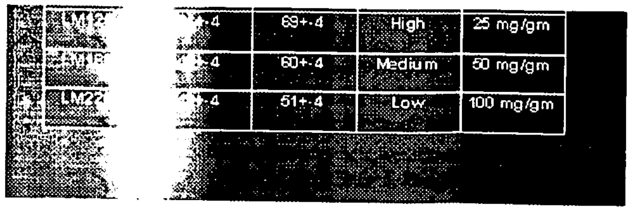


Figure 8 shows the gel mechanism fo[illegible]ctin. This involves joining carboxyl groups on adjacent chains with divalent ions, usually calci[illegible]sium. Again, this creates a "junction zone" which can be thought of as crystallized out of solutio[illegible]x" model for calcium alginate gels would also be valid for LM pectin gels.





LM12	-4	69+-4	High	25 mg/gm
LM18	-4	60+-4	Medium	50 mg/gm
LM22	-4	51+-4	Low	100 mg/gm

Figure 9 lists some parameters for 3 ty of LMC pectin. These three pectins are a homologous series, differing only in their degree of metho n. The "DFA" is the degree of free acid, or percent carboxyl groups available for cross link g with n. By definition, the LM12CG pectin is said to have **HIGH** calcium reactivity, meaning that it nee LESS m than the other two LMC pectins to make a good gel, all other factors being constant. This m es se, cause LM12CG has more acid groups along it's chain, therefore the statistical odds of a calciu ion be he right place at the right time are greater. LM22CG has only 50% acid groups along it's ch , the e statistical odds for a calcium ion to be in the right place at the right time are lower. To raise the stati dds, one must add more calcium to the LM22CG system, thus LM22CG needs more calcium than LN , and is said to be **LESS** calcium reactive. To demonstrate the magnitude of the difference in calciu rement, look at the last column of data. At 30% soluble solids, an LM12CG containing gel will n d abo ng of calcium ions for every gram of pectin. At 30% solids, the LM18CG gel will need about t e as alcium, and the LM22CG gel will need three or four times as much, to make the same firm s o he LM12CG with 25 mg per gram. Needless to say, only the LM12CG is actually intended r use a solids.

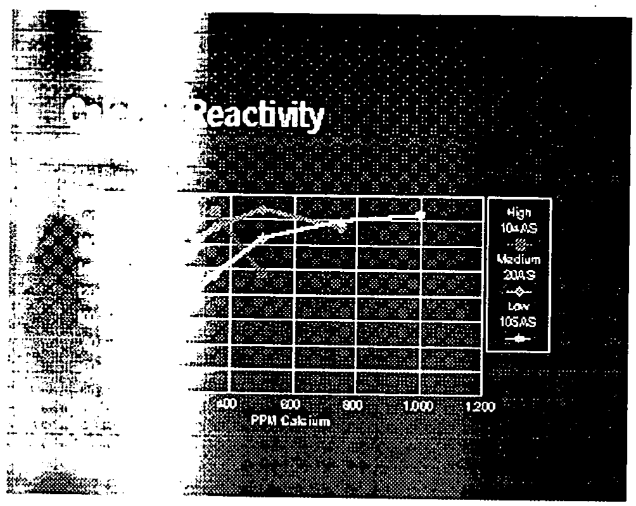


Figure 10 visually illustrates the relat between LM104AS, LM20AS, and LM105AS at 30% solids. Note that the calcium response cur ves of e tin "flatten out" at some point. This is known as **calcium saturation**, where an additio al incre calcium has no additional effect on the strength of the LM pectin gel. Unlike other calcium gell g hydr s such as sodium alginate, this saturation point is typical for all types of LM pectin.

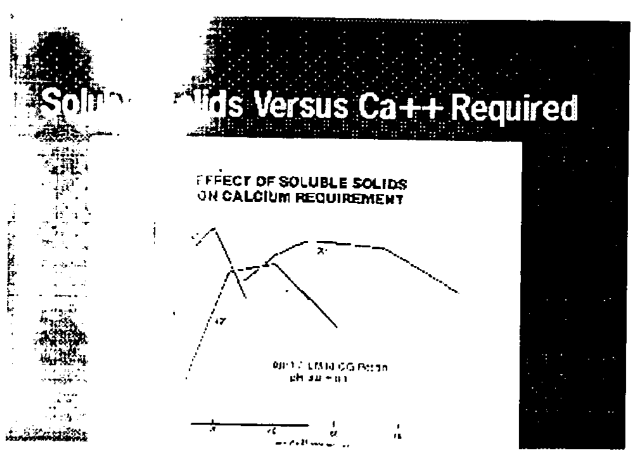
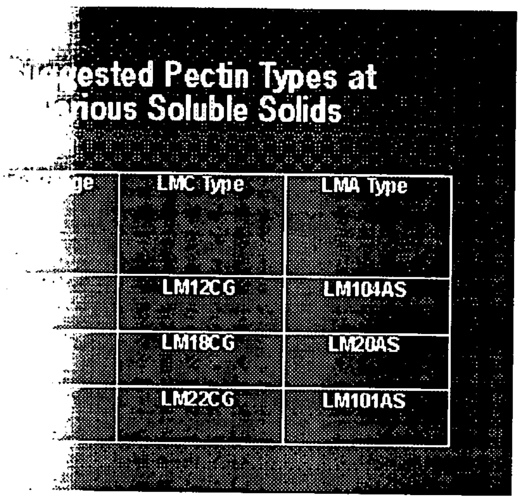
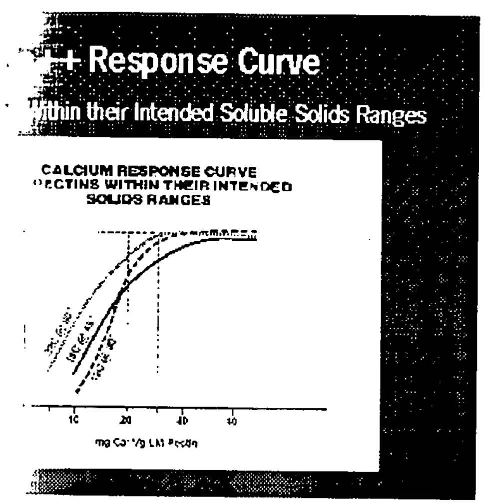


Figure 11 illustrates the effect of soluble s ids on the amount of calcium required to make a proper gel. In our lab, when we want to test an L A pectin for t's response to calcium, we prepare five or six small batches of gel. Each batch contains the same amount of p ectin, water, sugar, and buffer. The only difference between the six gels is the amount of calcium added. After 18 hours, we measure the firmness of each batch, and plot the data as gel strength versus calcium level. From Figure 11, one can see that at 30% solids with LM18CG pectin, about 40 to 100 mg calcium p r gram of p ctin are required to make a good gel. If we prepare the gels at 45% solids, the required calcium r e drops d wn to about 20 to 45 mg calcium per gram pectin. At 60% solids, the requirement drops further about 5 to 20 mg calcium per gram. With a given LM pectin, as the soluble solids goes up, the calcium re uirement goes down. Please also note that as the soluble solids goes up, the calcium "bandwidth", or the " ible workir g range" of the pectin becomes more narrow. This can limit you from using a high calcium rea ivity LM pe tin at high solids levels: the calcium "bandwidth" becomes too narrow, and you can't keep y r product w hin the required calcium range. Note that the "down" side of the calcium curve represents preg l, an apple auce like texture which one usually tries to avoid. Pregel will be explained in detail later.



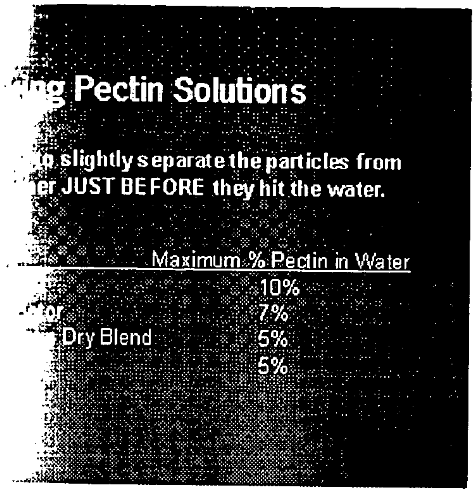
ge	LMC Type	LMA Type
	LM12CG	LM104AS
	LM18CG	LM20AS
	LM22CG	LM101AS

As a general rule, we recomm … cium reactivity LM pectins for use at low soluble solids, and low reactivity LM pectins for high … ds ranges. Figure 12 lists the typical LMA and LMC pectins, and their intended solids ranges.

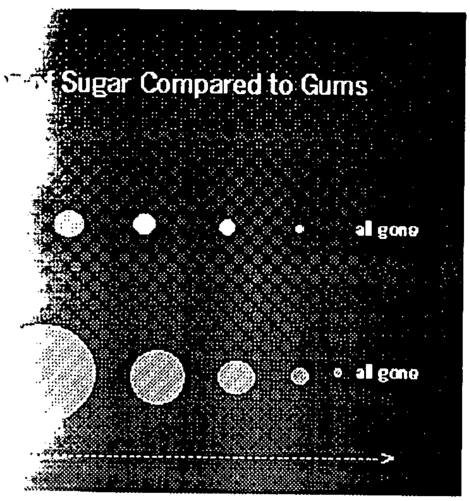


The idea of having several gr le … ctin, which all perform the same functions, is so the end user only has to remember one calciun … This is illustrated visually in Figure 13. The calcium response curve for LM12CG at 30% sc … as the response curve for LM18CG at 45% solids, which in turn

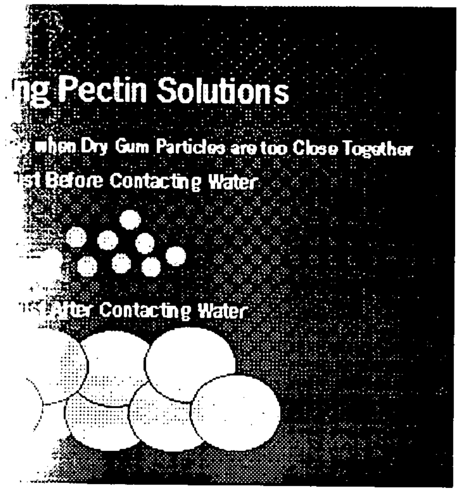
is the same for the LM22CG respo s e at 60% solids. We pair up the calcium reactivity with the soluble solids, so that the end user o y h mber one calcium response curve: that about 20 to 25 mg of calcium ions are needed for ery M pectin present in the formula, to ensure efficient use of the LM pectin.

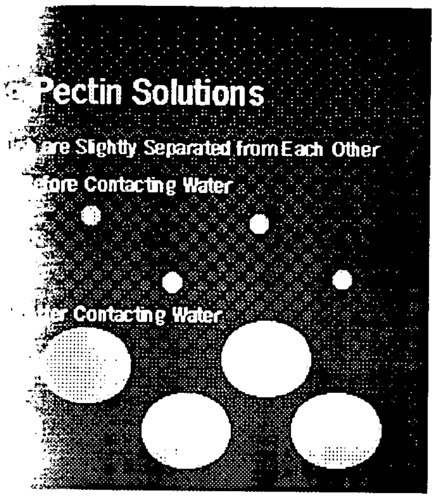


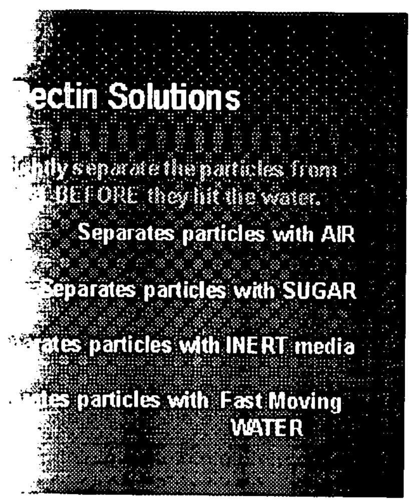
We will now take a break fro hnology to review the proper means of hydrating pectin. If you try to stir a teaspoon of pectin in vater, you will get one large, sticky lump floating around in your beaker. If you are patient, an vait several days, the lump will eventually dissolve and go completely into solution. Mos e the luxury of that much time to dissolve our pectin. This difficulty in dispersion holds pectin, but for all hydrocolloids.



The key to lump-free pectin h member the following: Separate the pectin particles from each other **BEFORE** they hit the s er. Figure 15 shows a comparison of the hydration of the sugar in your morning coffee versu particle enters the water, and begins to dissolve from the outside in. The sugar particle r with time as the molecules hydrate and float away, and within minutes all the sugar is disso other gums **DO NOT WORK THIS WAY!!!** When a pectin particle lifts the water, it rapi like a sponge and the particle swells to many times it's original size. I think of it as going *"S* s the water, becoming hundreds of times larger. When it has swelled to a certain size, the cules begin to unravel themselves from the outside surface, and float away from the particle, etely hydrated. If the pectin particles are right next to each other when they contact the water, o *"SPROINK"* at the same time, and weld themselves together into one large, slow to hydra ctin particles are all slightly separated from each other when they contact the water, then they oom to go through their initial expansion without getting stuck to a neighbor.



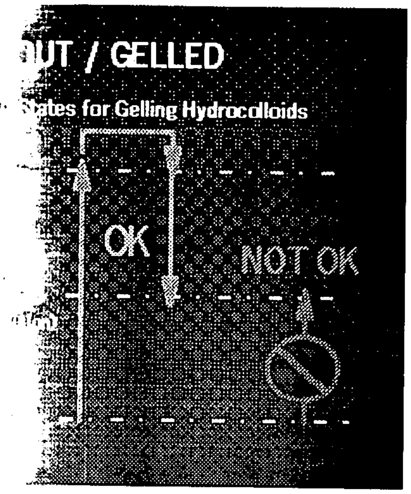




There are several ways to ach paration (Figure 16). The first is the use of a polymer
disperser, such as the Hercul ere, the pectin particles are separated by a stream of air just
before they contact the water. lending of 5 parts sugar to 1 part pectin. When this is
dispersed into water, the suga n't go "***SPROINK***") separate the pectin particles, allowing
the pectin to expand without c eighbor. Third is the use of non-solvents, such as vegetable
oil, glycerin, or 80% solids 42 non-solvents, the pectin particles are wetted and separated
from each other but cannot sv of high shear, where the rapidly moving water separates

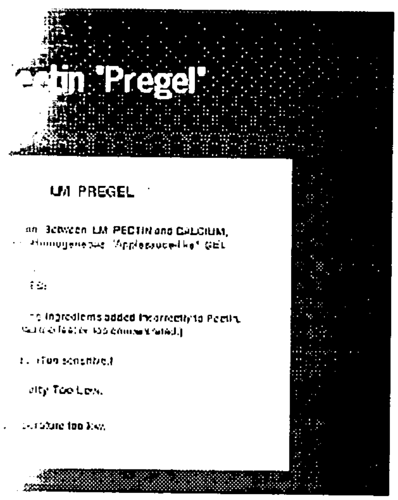
the gum particles. Also, if lum
lumps and ensure quick hydr
Cuisinart food processor, the

ie high level of mechanical work being done will break up
s typified by devices such as the Warring Blender, the
id the Clover Triblender.



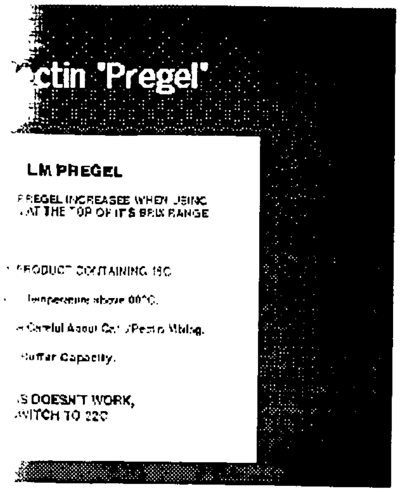
When you buy a drum of pect
is to put it completely into the
which I think of as being "hali
state directly into the gelled s
conditions. You must hydrate
the temperature, or adding c

precipitated state (Figure 17). The first thing you must do
) state, before you can induce it to go into the gelled state,
solution. Mother Nature will not allow you to go from the dried
r way, you **CANNOT** hydrate a gelling agent under gelling
g conditions, and then induce gelling conditions by lowering
akes to trigger your particular gelling agent.



LM pectin pregel is defined as
nonhomogeneous gel structu
cause of pregel is related to t
gets added too fast, or at the
one time in ten, the LM pecti
required. Also, certain applic
Very rarely, the cause is too l

etween the LM pectin and the calcium ions, resulting in a
pplesauce in texture (Figure 18). Nine times out of ten the
alcium is introduced to the LM pectin. Usually, the calcium
cess. or it's simply too concentrated when added. About
ve for the particular application, and a less reactive grade is
ves" are prone to pregel if their buffer capacity is too low.
ure.



For example, if you were to u Figure 19) in a product at 65% soluble solids, and if you encountered pregel, then you owing: First, make sure your process temperature was 80 degrees C or higher. Next, m using the proper order of addition of ingredients, which I will illustrate shortly. If these are is to switch to LM22CG, which is the next less calcium reactive LM pectin in the seri k the buffer capacity of my product, and if it was below 1.2%, I would add sufficient c citrate to bring it to at least 1.2% without changing the final pH of the product.

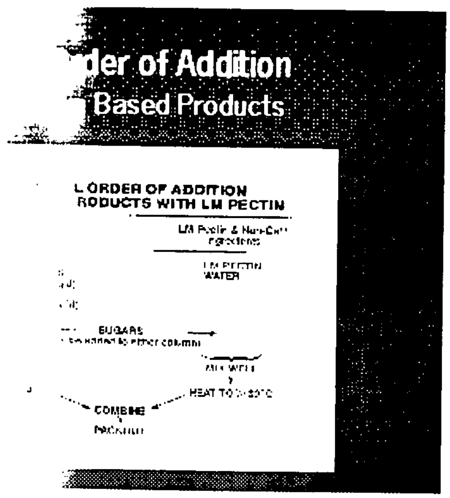
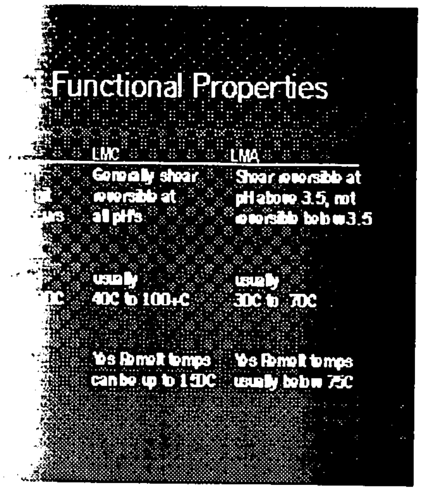
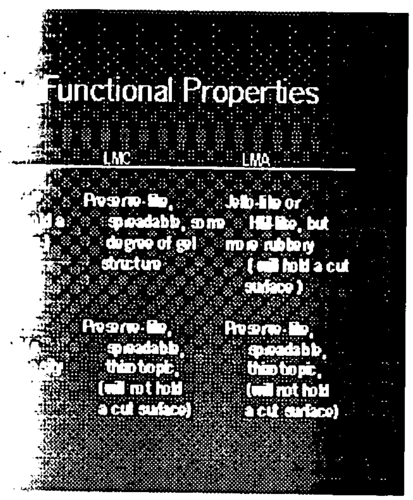


Figure 20 shows the ideal ord 1 pectin based products. It essentially comes down to this: Put all the calcium containing buffers in one pot on the stovetop, mix well, and heat to about 70 or 80 degrees C. P ectin into a Warring blender, and make a pectin solution. Put the solution into a second and also heat to 70 or 80 C. When both pots are up to temperature, pour one into th ix. The idea here is to dilute out the calcium in as much other material as possible, to on rate. The pectin is "diluted" (actually it's hydrated) in water as much as possible, a are heated to try to bring them above the gelling temperature of the system before they are gar contains virtually no calcium, it may be added to either pot or both pots, whatever is ually sugar is added to the fruit side, so as to osmotically equilibrate the system. That' re are some exceptions to this order of addition, but not many.

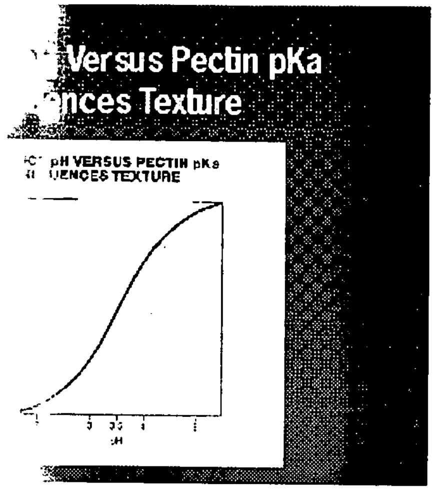


Figures 21 and 22 summariz(! differences between the three major types of pectin. HM pectin gels are not shear rev(ır of jelly with a spoon, you will break the gel, and it will not re-knit over time. Instead, it v ·e. LMC pectin is generally regarded as shear reversible over the whole pH range, while LN ·ersible at pH values of 3.4 or higher.

The setting temperature of aı be varied between the limits of 25C to 90C, by changing the DE of the pectin. An LMC ge een the limits of 40C to 100+C, while an LMA gel will generally set between 30C to ıal reversibility is concerned, HM gels are not thermally reversible (i.e., they don't m MC and LMA gels are thermally reversible, and LMA gels generally re-melt by the time .ated to 75C. LMC gels can have re-melt temperatures of up to 150C, so they can appear :rsible under atmospheric conditions.

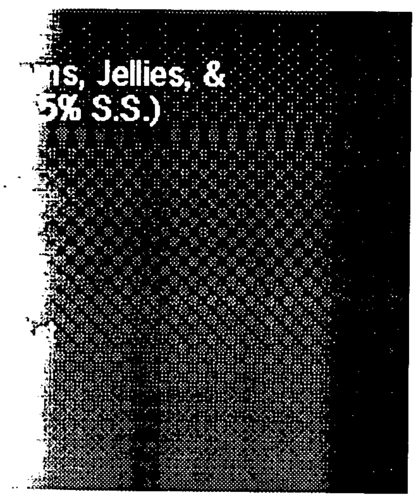


With regards to texture, HM ıewhat Jell-O-like texture, and will hold a cut surface. Above pH 3.5, HM pectin doesn't g. les some viscosity but no gel structure. LMC gels have a spreadable, preserve-like te: ase in rigid gel structure as the pH is lowered below 3.4, and they generally will flow at a c at pH values of 3.5 or higher have a very similar texture to LMC gels, with good spread: elow 3.4, LMA gels are Jell-O-like or HM pectin-like, but somewhat more "rubbery".



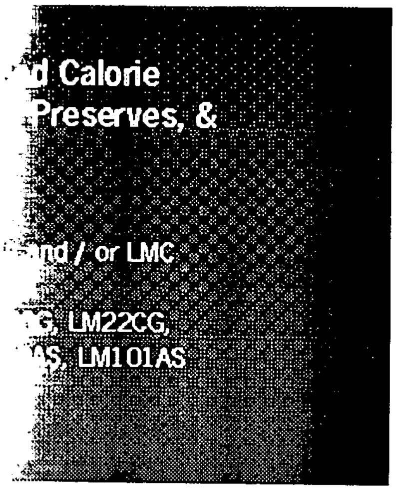
The reason for the texture of ing dependent on pH is shown in Figure 23. The pKa, or 50%
ionization pH, of pectin is at I is below 3.5, there are a predominance of non-dissociated
acid groups, which leads to m ng in the gel network. This gives rise to a more rigid, non-
shear reversible gel network. ve 3.5, then there are a predominance of ionized acid
groups, which leads to more c . This gives rise to a more spreadable, shear reversible gel
network.

AP OF HM AND LM PECTIN



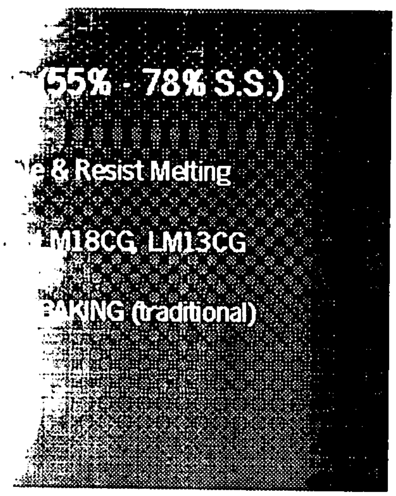
HM pectin is used for all tradi ntity jams, jellies, and preserves. These are made with a
soluble solids of 65%, a final generally contain 0.3% to 0.5% HM pectin. For the
manufacturer who is filling st to one pound glass jars, the suspension of the fruit is
critical. He fills the jars with 1 ilize the inside of the jar, yet he doesn't want the
strawberries floating up to the onsumers think they are being cheated if the jar has fruit on
the top half and what looks lik half. To keep the fruit evenly suspended, the jam producer
uses a rapid setting HM pecti oduct reaches the jar, it heats up the jar, and drops to 170F,
and the rapid set pectin imm , thus keeping the fruit evenly suspended in the jar.

At the other end of the scale, also filling his jars at 180F, but his filling machine tends to
whip some air into the hot liq on't like to see trapped air bubbles in jelly, as they think
something is wrong with it (s icer therefore uses slow setting HM pectin. This allows at
least fifteen minutes to go by product begins to set, which is plenty of time for all the air
bubbles to rise to the surface



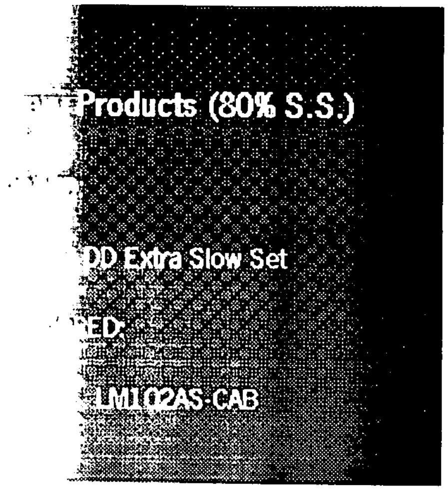
As soon as you move into th(
conditions, and you turn to L
represents half the calories c
with fruit and juice, and cont
60% soluble solids range, w
that HM pectin will **not** be re
reactivity LM pectin, and for
I recommend a 50%/50% mi.
pectin gel texture at these lc
jellies at 6% to 10% solids w
to any formula below 25% s(

ed calorie fruit spreads, you are outside of HM pectin gelling
educed calorie spread is 30% to 35% soluble solids, which
y product. Also, there are "conserves", which are made only
r corn syrups. The conserves are generally in the 50% to
ed edge" of gelling conditions for HM pectin, which means
ch. For the 30% soluble solids spreads, use a high calcium
nedium reactivity LM pectin. As far as texture is concerned,
, as this seems to give the best approximation to an HM
ven successfully made artificially sweetened jams and
I recommend that you add 0.1% to 0.4% locust bean gum
rm syneresis control.



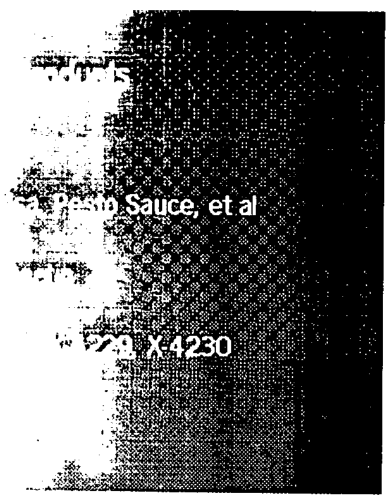
Traditional bakery jellies in t
gels are prone to syneresis
70%. If you want to make a
low as 50%, then you shou

ed on HM pectin, due to it's good thermal stability. These
heared, but this is only apparent at solids levels below
heat stable bakery filling at soluble solids of 70% to as
th LMC pectin.

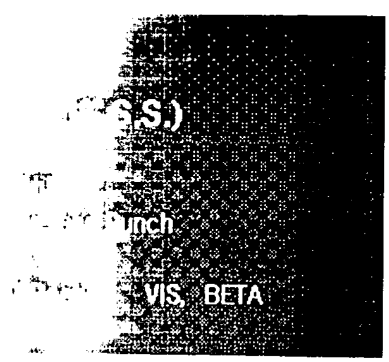


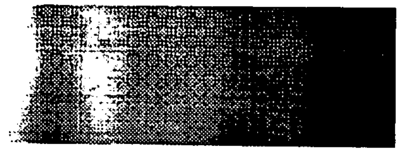
In the U.S., most candy is b… …ope, most candy is based on pectin. Pectin candy is a little
more technically challengin… …e advantages of much better flavor release, and it can be
cast directly into molds at 8… …ly, and demolded thirty minutes later. For a typical fruit
flavored pectin candy, one … …setting HM pectin, and would target on 80% final soluble
solids with a final pH of 3.5. … …) to 45 minutes at 180F to deposit the candy into molds.

For the "neutral" flavors, suc… …t, licorice, etc, a buffered LM pectin would be appropriate.
The buffer system is based … …final pH is around 4.2, so the final product does not taste
sour, and is therefore comp… …ors.

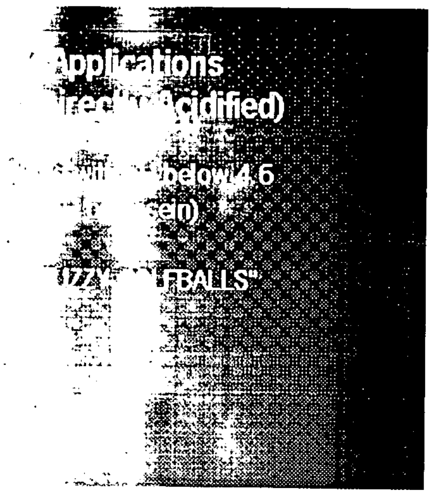


Because of it's spreadable … …heat stability. LMC pectin can be used in tomato based
products such as barbecue … …n alternative to modified food starch.

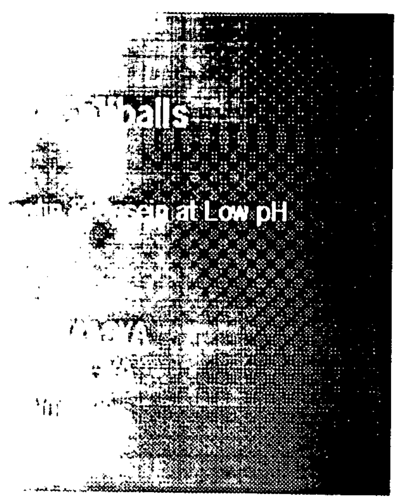




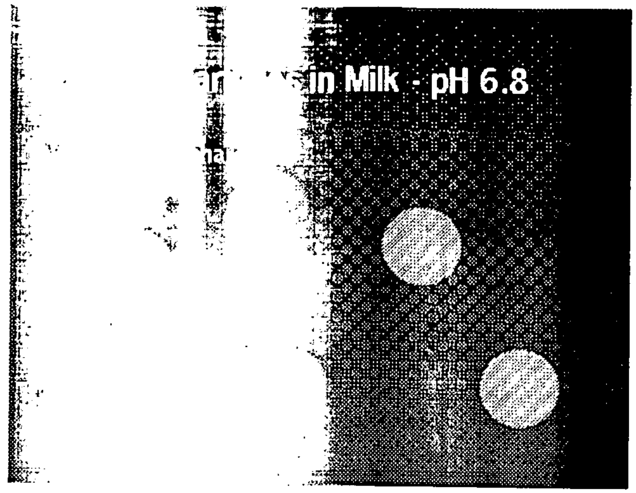
A typical beverage contains 1 sugar, and has a certain viscosity in the mouth as a result.
When you make the diet ver , you take out the 15% sugar, and you put in 15% more water
along with a tiny smidgen of The resulting beverage literally tastes as thin as water
because it is water! A tenth o in a et beverage can put back most of the texture you
lost when you removed the s ny s ificant calories. A dilute pectin solution will mimic
the Newtonian behavior of a



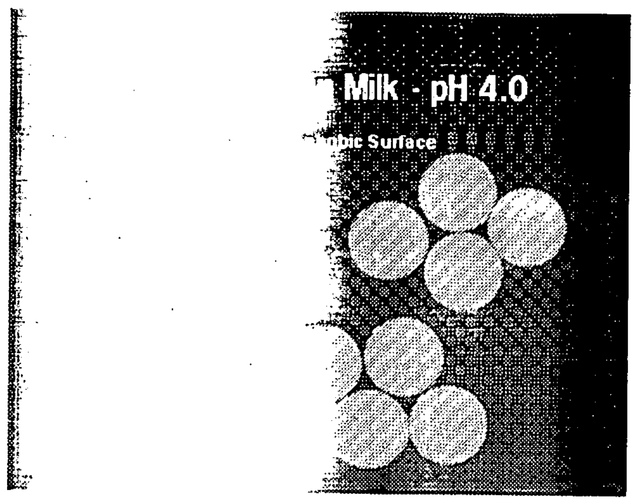
Pectin has another group of due it's ability to stabilize protein which is being
subjected to pH conditions b pH. I will refer to this as the *"fuzzy golf ball"* theory.



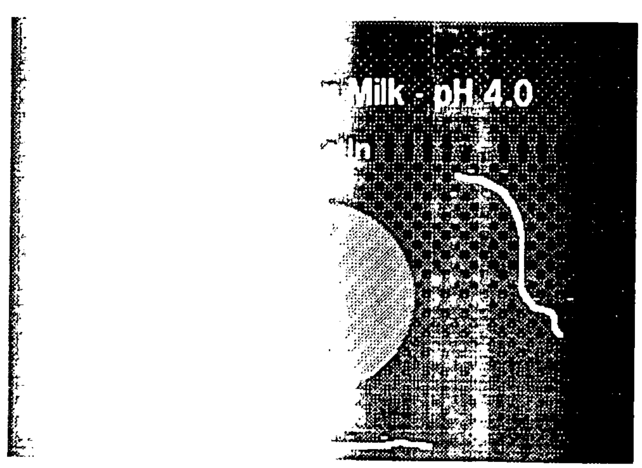
When you were little, did you uice into your milk to see what would happen? The result
is a rather nasty looking mix ickly drop to the bottom of the glass. Now we have a
way of making such a mixtu taste good, and be stable for months. Pectin can
stabilize juice / milk and othe s well as cultured milk products such as yogurt,
buttermilk, and sour cream. s:



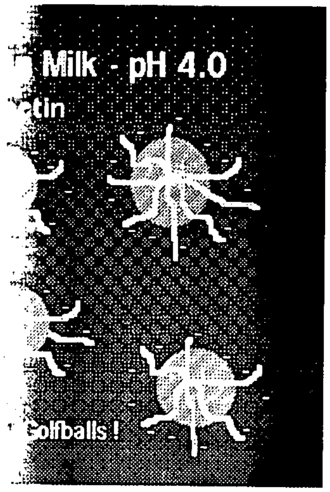
Milk is actually a suspension of particles, which are very small in size. At milk's ambient
pH of 6.8, the casein particles ge, and they repel each other. The Brownian motion of
the water molecules is sufficie icles in suspension indefinitely.

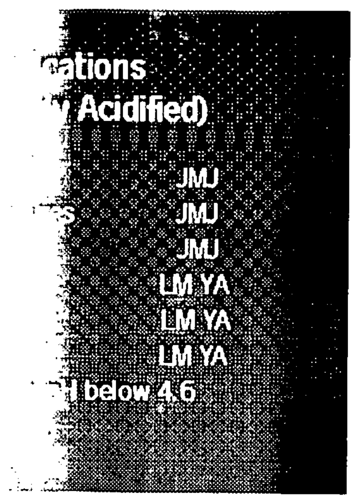


When the pH of milk is lowered by the action of microorganisms on lactose, the
casein particles lose their net there are still positive and negative areas on the
surface of each casein particle particle becomes zero as the pH is lowered below
about 4.6. When this happens to stick together in larger clumps, and Brownian
motion will not keep these lar they settle to the bottom of the container.

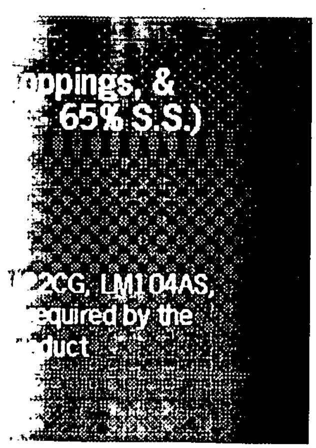


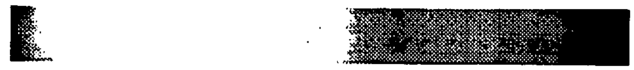
Pectin has a net negative charge 'n a low pH milk system, the negative pectin molecules will electrostatically stick to the pc ;ein particles, while avoiding the negative areas. If you visualize a casein particle as look :i the pectin can be compared to short pieces of yarn. The electrostatic complex of case looking like a golf ball coated with yarn, hence the name *"fuzzy golf ball"*.



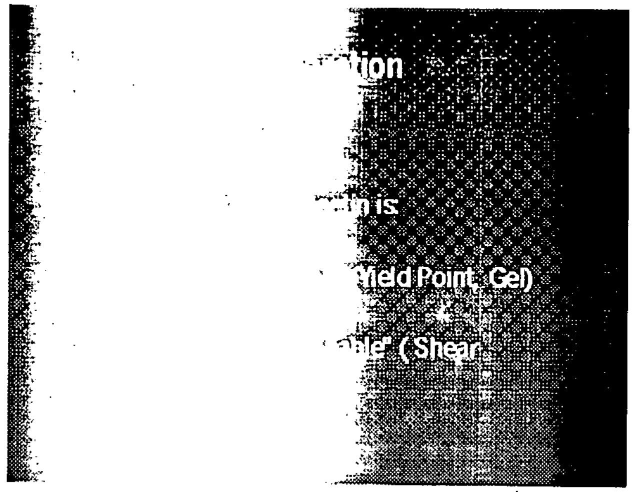


Pectin will also stabilize low pH ; milk. For directly acidified systems and for heat processed yogurt drinks, HM pe ultured products, LM pectin is more efficient.

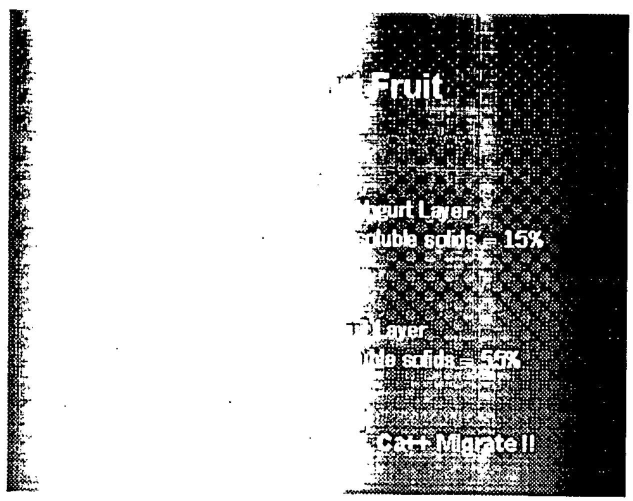




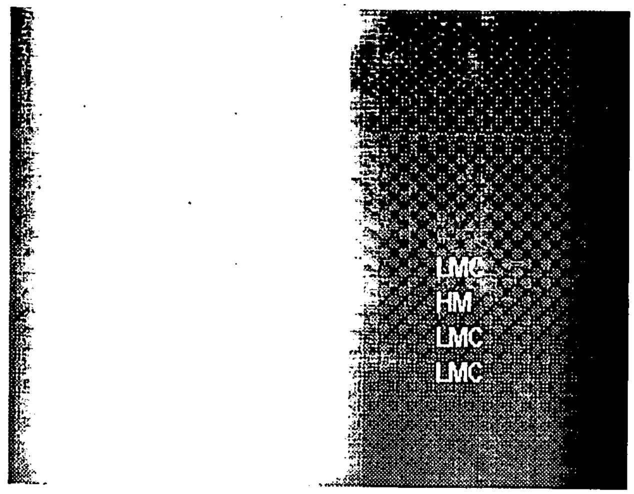
The last group of food applicatio ɔe cream toppings, variegate syrups, and related
items. Of these, yogurt fruit is pı technically.



Most yogurt fruit is packed into and these totes typically hold one thousand pounds
of fruit preparation or more. Th venly suspended throughout the container, because
the prep is pumped directly intc tes. In addition, there must be no tendency for
syneresis to occur as a result o receives when it is pumped out of the tote and
into the cups (i.e., it must be sh erfectly suited for this application.



Fruit on the Bottom yogurt pres allenges. When the 15% soluble solids white layer
is in contact with the ~55% sol notic difference causes water to migrate down into
the fruit layer, taking with it all he white layer (~1000 PPM). If the LM pectin in
the fruit layer is not at calcium is made, then the LM pectin reaches saturation
while it is under the yogurt, res r which is difficult to stir into the yogurt. We refer
to this hard fruit layer as a "hoc ucks" from occurring, one has to ensure that the
LM pectin is calcium saturated nade.



We have developed many Fat ! !ems based on our pectin technology.

I hope that this "Introduction to :nd enlightening for you. If you have any technical or application questions regardin. feel free to contact me:

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LANTS

Acids and their salts ser functions in foods that include the following:

1. Flavoring to prov ste and serve to intensify, enhance, blend of modify the f the product.
2. Reduction of the retard the growth of microorganisms and the germination of ncrease the lethality of the process.
3. Maintence or esta serving as buffering agents. Usually a combination of free re used.
4. Chelation of meta in minimizing lipid oxidation (Cu, Fe), reducing color char ng texture in some fruits and vegetables.
5. Alteration of th s including gels made from gums (pectin, carrageenan), and p
6. Interaction with ifiers to modify the structure of foods such as doughs, al ity of proteins, and to serve as an emulsifier in proc
7. Modification of tion in hard candy manufacturing.

ACIDULANTS

ACID	pKa
ACETIC	4.75
PHOSPHORIC	2.1, 7.? 12.3
CITRIC	3.08, 4. 5.4
LACTIC	3.86
HYDROCHLORIC	--
SULFURIC	--, 1.9
CARBONIC	6.4, 10.3
MALIC	3.4, 5.1
SUCCINIC	4.2, 5.6
TARTARIC	3.2, 4.?
FUMARIC	3.03, 4.
ADIPIC	4.43, 4.
GLUCONIC	3.60
PYROPHOSPHORIC	0.9, 1.5, 5.8, 8.?

MAJOR DIFFERENCES IN ACIDU

1. FLAVOR
2. ACIDITY
3. METAL CHELATING A
4. ANTIMICROBIAL AC
5. SOLUBILITY
6. HYDROSCOPICITY
7. COST

ACIDULANT	APPLICATIO	ON
Citric acid	Accounts f of all aci used.	rol, r, dant, st
	Cultured da products	te for ion
	Processed	rotein sify
	Evaporated	e to heat
	Honey	lization
Phosphoric acid	Accounts f	to
Acetic acid (vinegar)	Mayonnaise sauces, p dressings	rol, fe
Succinic acid	Bread doug	s ity
	Gelatin po	ed pH nt to
Adipic acid	Gelatin p	rol to xture
	Baking po	g acid
	Jams, jel	ol for el

	Fruit proc	s
	Processed	erant er
	Meringue	g aid terant)
Tartaric acid	Baking po	ng acid
	Fruit but jams, she jellies	pH
	Hard cand	lation

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